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PREFERENTIAL SORPTION VERSUS PREFERENTIAL PERMEABILITY IN PERVAPORATION*

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Summary

Transport of liquids by pervaporation takes place by a solution—diffusion mechanism. In order to investigate the "solution part" of this transport model, preferential sorption has been compared with preferential permeability. Sorption equilibria and pervaporation experiments for the systems water—ethanol—cellulose acetate, water—ethanol—polyacrylonitrile and water—ethanol—polysulfone have been investigated. Theoretical values of preferential sorption have been derived from Flory—Huggins thermodynamics, extended with concentration dependent interaction parameters. These calculated sorption values show a reasonable agreement with experimental values. The large difference in molar volumes between water and ethanol determines the preferential sorption of water in these systems to a great extent, and this effect increases with decreasing swelling value. Comparison of preferential sorption experiments with pervaporation experiments indicates that, apart from the effect of differences in diffusivity for the permeating components, preferential sorption contributes to a major extent to selective transport

Introduction

In most membrane processes transport of molecules takes place in the direction of decreasing chemical potential. In pervaporation, the driving force for transport is the concentration difference across the membrane. The transport process can be divided into three steps, (i) sorption into the membrane at the upstream side, (ii) diffusion through the membrane, and (iii) desorption into a vapour phase at the downstream side. The separation mechanism of pervaporation is a solution—diffusion mechanism [1—4], i.e., the permeation rate is a function of solubility and diffusivity. Solubility is a thermodynamic property and diffusivity is a kinetic property, both affecting selectivity. In the case of a liquid mixture, separation is obtained because the membrane has the ability to transport one component more readily than the other even if the driving forces are equal. Hence, prediction of selectivity is

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often difficult because there will be in general a coupling of fluxes, i.e., the permeation rate of one component can be changed by the presence and movement of the other component. In a recent article [4] a solution—diffusion model has been developed for the permeation of a liquid mixture through a polymeric membrane taking into account coupling of fluxes.

The objective of this paper is to investigate the thermodynamic aspects of the membrane separation process, by comparing preferential sorption of a water—ethanol mixture by a polymeric membrane with preferential permeability through that membrane.

Aptel [5] showed that for systems with polyvinylpyrolidone—polytetrafluoroethylene as membrane material and various binary liquid mixtures, the component that was sorbed preferentially was also transported preferentially. Even the occurrence of an inversion in selectivity was in agreement with their sorption experiments.

Our investigation can be divided into two parts:

(a) the thermodynamics of preferential sorption;

(b) a comparison of preferential sorption versus preferential permeability.

Preferential or selective sorption is given by the difference in composition of a binary liquid mixture inside the polymeric membrane, and outside in the liquid feed mixture. Theoretical values on preferential sorption have been derived from Flory—Huggins thermodynamics [6] using concentration dependent interaction parameters. To improve the agreement between experimental and theoretical data on preferential sorption Pouchlý [7,8] introduced a second-order interaction parameter, the ternary parameter g_T. Another way of describing second-order effects is by taking the interaction parameters to be concentration dependent. In this paper we will follow the latter approach.

Experimental data on preferential sorption have been obtained by separating the sorbed liquid quantitatively from the membrane phase by a distillation technique. These experimental data will be compared with the theoretical values. The following polymers have been studied: cellulose acetate (CA), polyacrylonitrile (PAN) and polysulfone (PSf), while water—ethanol was used as the liquid mixture. Except for equilibrium sorption measurements, pervaporation experiments have also been performed. The selectivity in pervaporation will be compared with the preferential sorption data, and the results will be discussed in terms of the solution—diffusion mechanism.

Theory

The equilibrium between a polymeric membrane (index 3) and a binary mixture of nonsolvents (indices 1 and 2) can be considered as an osmotic equilibrium. Preferential sorption occurs when the composition of the binary liquid mixture inside the polymer is different from that outside, in the liquid feed mixture. The index 1 is given to the component that is sorbed preferentially by the polymer. If we denote the concentration of a component of a binary liquid mixture in the polymeric phase by

$$u_i = \frac{\phi_i}{\phi_1 + \phi_2} = \frac{\phi_i}{1 - \phi_3} \qquad i = 1, 2 \tag{1}$$

and the concentration (volume fraction) in the liquid phase by v_i then the preferential sorption ϵ is given by [7]

$$\epsilon = u_1 - v_1 = v_2 - u_2 \tag{2}$$

The condition for equilibrium between the two phases, the binary liquid phase and the ternary polymer phase, are expressed by equality of the chemical potentials in the two phases. The polymer-free phase is denoted with the superscript o and the ternary (membrane) phase with the superscript m. At equilibrium we have:

$$\Delta\mu_1^{\circ} = \Delta\mu_1^{m} + \Pi V_1 \tag{3}$$

$$\Delta\mu_2^{\circ} = \Delta\mu_2^{m} + \Pi V_2 \tag{4}$$

The chemical potentials can be obtained from Flory—Huggins thermodynamics [6]. The Gibbs free energy of mixing of a ternary system is given by

$$\frac{\Delta G_{mix}}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + g_{12}(u_2) n_1 \phi_2 + g_{13}(u_2, \phi_3) n_1 \phi_3 + g_{23}(u_1, \phi_3) n_2 \phi_3 \tag{5}$$

The indices 1 and 2 again refer to the nonsolvents, and index 3 to the polymer; n_i and ϕ_i are the mole fraction and volume fraction of component i, respectively. The binary interaction parameters g_{12}, g_{13} and g_{23} are assumed to be concentration-dependent. In case these parameters are independent of concentration, the g parameters equal the χ parameters. (In the original Flory—Huggins theory the χ parameters are concentration-independent [6].) Differentiation of eqn. (5) to n_1 and n_2, respectively, yields the following equations for the chemical potentials of components 1 and 2 in the polymer phase

$$\frac{\Delta\mu_1^{m}}{RT} = \ln\phi_1 + \phi_2 \left(1 - \frac{V_1}{V_2}\right) + \phi_3 \left(1 - \frac{V_1}{V_3}\right) + (g_{12}\phi_2 + g_{13}\phi_3)(\phi_2 + \phi_3) - u_1 u_2 \phi_2 \frac{\partial g_{12}}{\partial u_2} - g_{23} \frac{V_1}{V_2} \phi_2 \phi_3 - u_1 u_2 \phi_3 \frac{\partial g_{13}}{\partial u_2} - \phi_1 \phi_3^2 \frac{\partial g_{13}}{\partial \phi_3} + \frac{V_1}{V_2} u_2^2 \phi_3 \frac{\partial g_{23}}{\partial u_1} - \frac{V_1}{V_2} \phi_2 \phi_3^2 \frac{\partial g_{23}}{\partial \phi_3} \tag{6}$$

$$\frac{\Delta u_2^{m}}{RT} = \ln\phi_2 + \phi_1 \left(1 - \frac{V_2}{V_1}\right) + \phi_3 \left(1 - \frac{V_2}{V_3}\right) + \left(g_{12} \frac{V_2}{V_1} \phi_1 + g_{23}\phi_3\right)(\phi_1 + \phi_3)$$

$$- \frac{V_2}{V_1} u_1^2 \phi_2 \frac{\partial g_{12}}{\partial u_2} - g_{13} \frac{V_2}{V_1} \phi_1 \phi_3 + \frac{V_2}{V_1} u_1^2 \phi_3 \frac{\partial g_{13}}{\partial u_2}$$

$$- \frac{V_2}{V_1} \phi_1 \phi_3^2 \frac{\partial g_{13}}{\partial \phi_3} - u_1 u_2 \phi_3 \frac{\partial g_{23}}{\partial u_1} - \phi_2 \phi_3^2 \frac{\partial g_{23}}{\partial \phi_3} \tag{7}$$

According to the Flory—Huggins thermodynamics, the Gibbs free energy of mixing for the binary phase is given by eqn. (8) (where x_i is the mole fraction of component i in the binary liquid)

$$\frac{\Delta G_m}{RT} = x_1 \ln v_1 + x_2 \ln v_2 + g_{12}(v_2)\, x_1 v_2 \tag{8}$$

Differentiation with respect to x_1 and x_2 yields eqns. (9) and (10)

$$\frac{\Delta \mu_1^\circ}{RT} = \ln v_1 + \left(1 - \frac{V_1}{V_2}\right) v_2 + g_{12}\, v_2^2 - v_1 v_2^2 \frac{\partial g_{12}}{\partial v_2} \tag{9}$$

$$\frac{\Delta \mu_2^\circ}{RT} = \ln v_2 + \left(1 - \frac{V_2}{V_1}\right) v_1 + \frac{V_2}{V_1} g_{12} v_1^2 + \frac{V_2}{V_1} v_2 v_1^2 \frac{\partial g_{12}}{\partial v_2} \tag{10}$$

Assuming $V_1/V_3 \approx V_2/V_3 \approx 0$ and $V_1/V_2 = l$, substitution of eqns. (6), (7), (9) and (10) in eqns. (3) and (4) and elimination of Π gives

$$\ln\left(\frac{\phi_1}{\phi_2}\right) - \ln\left(\frac{v_1}{v_2}\right) = (l-1) \ln \frac{\phi_2}{v_2} - g_{12}(u_2)[\phi_2 - \phi_1] - g_{12}(v_2)[v_1 - v_2]$$

$$- \phi_3 (g_{13} - l g_{23}) + u_1 \phi_2 \frac{\partial g_{12}}{\partial u_2} - v_1 v_2 \frac{\partial g_{12}}{\partial v_2}$$

$$+ \phi_3 u_1 \frac{\partial g_{13}}{\partial u_2} - \frac{V_1}{V_2} u_2 \phi_3 \frac{\partial g_{23}}{\partial u_1} \tag{11}$$

Krigbaum [9] used a different coefficient for expressing the preferential sorption, namely the composition ratio CR ($CR \equiv \phi_1/\phi_2\,(v_1/v_2)^{-1}$ and $\ln CR = \ln(\phi_1/\phi_2) - \ln(v_1/v_2)$). The preferential sorption coefficient ϵ and the composition ratio CR are directly related to each other,

$$\epsilon = \frac{(CR-1) v_1 v_2}{[1 + (CR-1) v_1]} \tag{12}$$

The left hand side of eqn. (11) is equal to the logarithm of the composition ratio. One can see from eqn. (11) that this expression for the preferential sorption does not contain derivatives of g_{13} and g_{23} with respect to ϕ_3 anymore, while in equations for the osmotic pressure these derivatives are present.

If the interaction parameters are assumed to be concentration independent, eqn. (11) reduces to the same equations as have been derived by Scott [10] for systems with $l=1$ and by Krigbaum [9] for systems with $l \neq 1$.

From eqn. (11) the preferential sorption can be calculated numerically if the interaction parameters and their partial derivatives, the ratio of the molar volumes l and the volume fraction of polymer ϕ_3 (or the overall sorption) are known.

Evaluation of the binary interaction parameter g_{12}

In a recent article [4] it was shown that, if data on excess free energy of mixing are available $g_{12}(v_2)$ (or $g_{12}(u_2)$) can be calculated according to eqn. (13)

$$g_{12} = \frac{1}{x_1 v_2}\left[x_1 \ln \frac{x_1}{v_1} + x_2 \ln \frac{x_2}{v_2} + \frac{\Delta G^E}{RT}\right] \tag{13}$$

This method of calculating g_{12} values has also been used by others [11,12].

For many liquid mixtures the thermodynamic excess functions are available. The g_{12} function for ethanol—water has been calculated from literature data on ΔG^E taken from Westmeier [13]. This function, written as a fourth grade polynomial relation [4], is given by eqn. (14)

$$g_{12}(v_2) = 0.9820 - 1.3483\, v_2 + 4.15\, v_2^2 - 3.3116\, v_2^3 + 0.8897\, v_2^4 \tag{14}$$

For the liquid mixture in the polymer, v_2 has to be replaced by u_2. This $g_{12}(u_2)$ function is assumed to be independent of the polymer concentration. The derivatives of g_{12} to v_2 and u_2 can easily be obtained from eqn. (14).

Evaluation of the binary parameters g_{13} and g_{23}

Interaction parameters between a polymer and a nonsolvent can be determined experimentally by equilibrium swelling measurements, as has been described previously [4]. For the system studied the swelling measurements and interaction parameters are given in Table 1.

The parameters given in the last column of Table 1 are binary parameters. In order to consider second order or ternary effects the g_{13} and g_{23} parameters are assumed to be concentration dependent, i.e., g_{13} and g_{23} are functions of u_i ($i = 1, 2$) and ϕ_3. We will use such a mathematical expression for these parameters that if the concentration u_2 in the polymer increases, g_{13} will increase, and if u_1 increases, g_{23} will increase. Furthermore, if the polymer concentration increases both g_{13} and g_{23} will increase.

$$g_{13} = g_{13}(u_2 \to 0) + a u_2 + b[\phi_3 - \phi_3(u_2 \to 0)] \tag{15}$$

$$g_{23} = g_{23}(u_1 \to o) + c u_1 + d[\phi_3 - \phi_3(u_1 \to 0)] \tag{16}$$

For the limiting cases $u_2 \to 0$ and $u_1 \to 0$ eqns. (15) and (16) reduce to $g_{13} = g_{13}(u_2 \to 0) = \chi_{13}$ and $g_{23} = g_{23}(u_1 \to 0) = \chi_{23}$. The values of the constants $g_{13}(u_2 \to 0)$, $g_{23}(u_1 \to 0)$, $\phi_3(u_2 \to 0)$ and $\phi_3(u_1 \to 0)$ have been given in Table 1.

TABLE 1

Solubility and interaction parameters of water (component 1) and ethanol (component 2) in the polymers (3) cellulose acetate (CA), polyacrylonitrile (PAN) and polysulfone (PSf)

Polymer	Penetrant	Solubility (g penetrant/100 g dry polymer)	Volume fraction of polymer[a]	χ[b]
CA	water	14.3	0.84	1.4
PAN	water	8.9	0.91	1.8
PSf	water	0.1	0.999	5.9
CA	ethanol	21.5	0 74	1.1
PAN	ethanol	0.4	0.994	4.2
PSf	ethanol	2.3	0.96	2.5

[a] Indicated as $\phi_3(u_2 \to 0)$ or $\phi_3(u_1 \to 0)$, respectively, in eqns. (15) and (16).
[b] Indicated as $g_{13}(u_2 \to 0)$ or $g_{23}(u_1 \to 0)$, respectively, in eqns. (15) and (16).

The molecular interpretation of the magnitudes of the constants a, b, c and d is left for future study. These coefficients can be chosen in such a way as to improve the agreement between theory and experiment, as we will see later on

Experimental

Materials

Cellulose acetate (E 398-3) was obtained from Eastman Chemicals, polysulfone (P 3500) from Union Carbide and polyacrylonitrile (T 75) from DuPont. The solvents used were of analytical grade.

Membrane preparation

Polymer solutions were prepared by dissolving the polymer in a suitable solvent. The membranes were prepared by casting the polymer solution upon a glass plate and allowing the solvent to evaporate in a nitrogen atmosphere. The membranes used were completely transparant except for that consisting of polyacrylonitrile.

Swelling measurements

Dried strips of polymeric membrane (about 0.3 g) were immersed in different conical flasks containing water—ethanol mixtures of different compositions. The flasks were placed in a thermostat bath at 20°C. After 24 hours the strips were removed, pressed between a tissue paper and weighed in a closed flask. This procedure was continued until no further weight increase was observed. The solubility has been expressed as a relative weight increase (g penetrant/100 g dry polymer).

Pervaporation

The pervaporation experiments were carried out as described previously [14]. Vacuum at the downstream side was maintained at a pressure of 13.3 Pa

(0.1 mmHg) by a Crompton—Parkinson vacuum pump. The pressure was measured by an Edwards piranhi gauge. The experiments were carried out for eight hours. A product sample was taken every hour and generally steady-state conditions were reached in about three hours. The thickness of the homogeneous membranes was about 20 μm. The temperature of the liquid feed mixture was 20°C.

Product analysis

Analysis of binary ethanol—water mixtures was performed on a Varian model 3700 gaschromatograph fitted with a chromosorb 60/80 column and equipped with a thermal conductivity detector. For low ethanol concentrations (0—5%) a flame ionization detector was used.

Analysis of the binary liquid mixtures inside the polymeric membrane

The composition of the liquid mixture in the polymeric membrane was determined by a distillation technique as described by Patat [15]. The experiments were carried out with the apparatus given in Fig. 1. The apparatus was flushed thoroughly with nitrogen before the experiments were started. The polymeric membrane was immersed in a conical flask containing the binary ethanol—water mixture. After sorption equilibrium, which can be controlled by repeated weighing, the membrane sample was pressed between tissue paper and immediately put in tube 1. The closed tube 1 was cooled with liquid nitrogen and installed in the apparatus. The system was brought to a pressure of about 1.3 Pa (0.01 mmHg) while tube 1 was still cooled. After about 5—10 minutes, valve 5 was closed, tube 2 was cooled with liquid nitrogen (the level up to which cooling is performed is indicated by the dashed line) and tube 1 was heated with boiling water. Within 10—30 seconds, the liquid inside the membrane started to boil and the vapour was condensed in tube 2. After about 10—15 minutes the experiment was stopped because no more liquid could be removed from the membrane. This was checked in two ways: by

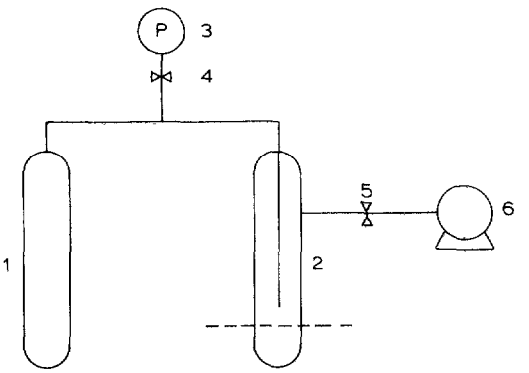

Fig. 1. Apparatus to determine the composition of the liquid mixture inside the polymer; 1, 2 — collecting tubes, 3 — piranhi gauge, 4, 5 — valves, 6 — vacuum pump.

following the pressure during the experiment and by performing experiments for longer periods of time. The amount of liquid inside the membrane could be determined by simply weighing, while the composition was determined by gas chromatography.

The experimental error depends on the amount of liquid sorbed by the membrane. The maximum amount of liquid sorbed in a PSf membrane is about 3%, while for CA membranes up to 25% was sorbed. The error in the mass balance is about 5% for polysulfone systems.

Results and discussion

The experimental total sorption values of ethanol—water mixtures in cellulose acetate, polysulfone and polyacrylonitrile are given in Fig. 2. Figure 2 demonstrates clearly the difference in thermodynamic behaviour between the different polymers and ethanol—water mixtures; low swelling values in PSf and PAN and much higher values in CA are observed. PSf and PAN show opposite behaviour, hardly any water sorption in PSf while PAN shows hardly sorption for ethanol. The solubility of ethanol—water mixtures in CA passes through a maximum at about 65% ethanol in the feed.

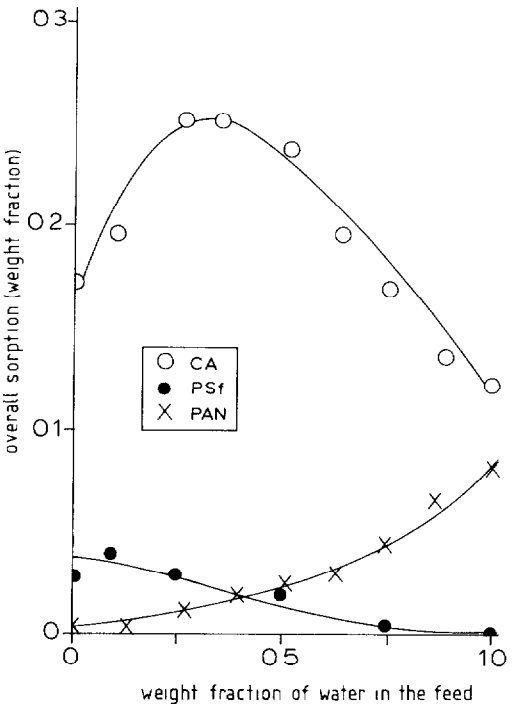

Fig. 2. Total sorption as a function of the water content in the water—ethanol liquid feed mixture for different polymers at 20°C.

Values for the preferential sorption have been determined experimentally and theoretically. The theoretical values can be calculated from eqn. (11). Equation (11) shows that preferential sorption depends on the difference in molar volumes of the two penetrants, the affinity of both components towards the polymer and the mutual interaction between the two penetrants.

The effect of the difference in molar volume has its origin in the combinatorial entropy, and this effect upon the preferential sorption increases if the difference in molar volume increases, and if the polymer concentration increases. The component with the smaller molar volume will be sorbed preferentially. For water—ethanol the ratio of the molar volumes $l(= V_1/V_2)$ is 0.31, which means that water will be sorbed preferentially.

Positive values of the term containing the interaction parameters with respect to the polymer $(lg_{23} - g_{13})$ will favour the preferential sorption of component 1; this effect also depends on the polymer concentration. For the systems studied this value is negative. Hence, this term contributes to selectivity towards component 2 (ethanol).

The influence of g_{12} on the preferential sorption depends on the concentration in the binary liquid phase and on the sign of the g_{12} interaction parameter. In the case of water—ethanol the interaction parameter g_{12} has a positive value over the entire composition range. This implies that the term $g_{12}(v_2 - v_1)$ has a positive effect on the preferential sorption of water for high ethanol feed concentrations $(v_2 > v_1)$, while it has a negative effect for high water feed concentrations $(v_1 > v_2)$. The same applies for $g_{12}(\phi_1 - \phi_2)$, but the effect of this term is much smaller because ϕ_1 and ϕ_2 are smaller for the systems studied compared to v_1 and v_2.

The influence of the derivatives of g_{13} and g_{23} with respect to u_2 and u_1, respectively, depends on the magnitudes of the constants a and c (see eqns. 15 and 16). The term containing the derivative $\partial g_{12}/\partial v_2$ has a positive effect on the preferential sorption of water, while the term with $\partial g_{12}/\partial u_2$ has a negative effect, the latter being smaller than the former.

When neglecting the concentration dependency of the interaction parameters, it can be deduced from eqn. (11) that for the limiting case $\phi_3 \to 1$, the liquid mixture inside the polymer consists almost exclusively of the component with the smaller molar volume.

Some numerical examples will demonstrate the influence of the different factors (difference in molar volume, difference in affinity towards the polymer and the mutual interaction between ethanol and water) on the preferential sorption applied to ethanol—water mixtures. Figure 3 gives the preferential sorption of ethanol—water for different polymer concentrations assuming equal and constant polymer—nonsolvent parameters ($\chi_{13} = \chi_{23} = 1.0$). For g_{12} (water—ethanol) eqn. (14) has been used. It is obvious that the effect of the difference in molar volume on the preferential sorption of water becomes stronger if the polymer concentration increases.

Figure 4 is an example of an opposite effect. The smaller molar volume of water, which favours the preferential sorption of water, is opposed by the

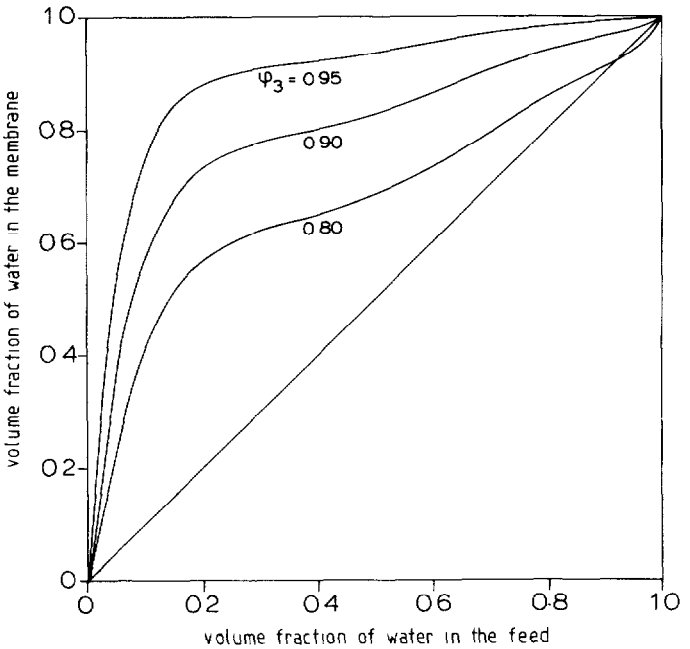

Fig. 3. Preferential sorption in a ternary system water—ethanol—polymer for different polymer concentrations ($\phi_3 = 0.95$; $\phi_3 = 0.9$; $\phi_3 = 0.8$). Other parameters: $\chi_{13} = \chi_{23} = 1.0$; $g_{12} = g_{12}(u_2)$ (see eqn. 14); $l = 0.31$.

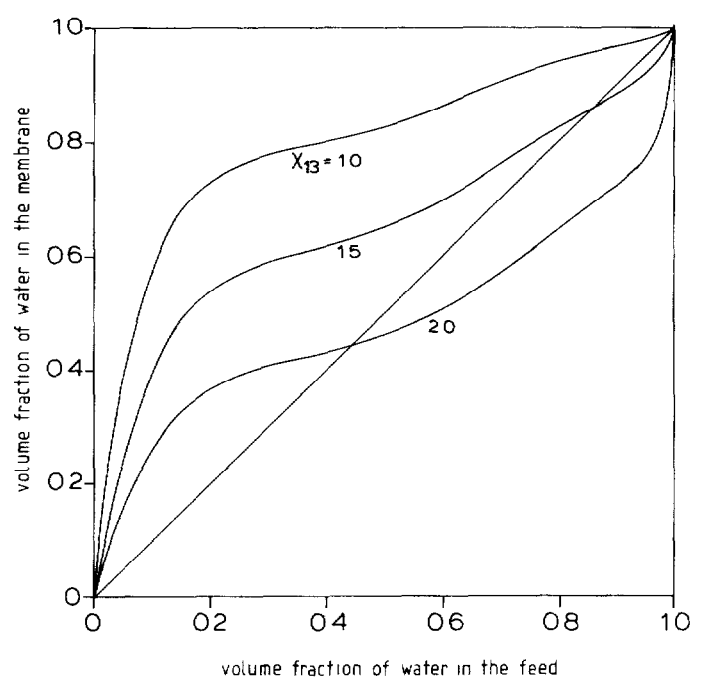

Fig. 4. Preferential sorption in a ternary system water—ethanol—polymer for different values of χ_{13} ($\chi_{13} = 1.0$; $\chi_{13} = 1.5$; $\chi_{13} = 2.0$). Other parameters: $\chi_{23} = 1.0$; $g_{12} = g_{12}(u_2)$ (see eqn. 14); $l = 0.31$; $\phi_3 = 0.90$

small mutual affinity of water and polymer. When the χ_{13} parameter increases, keeping χ_{23} constant, the preferential sorption of water decreases and even an inversion in preferential sorption can be observed. Furthermore the lower curve (χ_{13} = 2.0) of Fig. 4 demonstrates clearly the influence of the g_{12} parameter on the preferential sorption: g_{12} is positive over the entire composition range (see eqn. 14), and the contribution to the preferential sorption is positive for low concentrations of water in the feed, while it has a negative effect for high concentrations of water in the feed.

In case of polysulfone and polyacrylonitrile as membrane materials, the polymer concentration, ϕ_3, is quite high (see Fig. 2). For the system water—ethanol—polyacrylonitrile we expect a large preferential sorption for water, because the component with the smaller molar volume (water) has also a larger affinity towards the polymer (see Table 1 and Fig. 2). For the system water—ethanol—polysulfone, the preferential sorption for water due to the effect of the smaller molar volume is counteracted by the very small affinity of water to polysulfone. In the next section we will see how the experimental and theoretical data agree.

The system water—ethanol—cellulose acetate (sorption results)

In Fig. 5 the theoretical values for the preferential sorption calculated according to eqn. (11) with constant interaction parameters ($g_{ij} = \chi_{ij}$) and with concentration dependent interaction parameters, together with the experimental values are given as a function of the water concentration in the feed. The experimental values show that water is sorbed preferentially over the entire composition range. The preferential sorption increases with decreasing water concentration in the feed mixture.

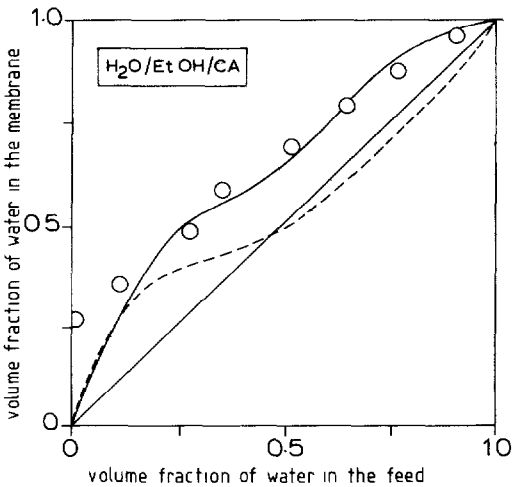

Fig. 5. Experimental values (○) for the preferential sorption (expressed as volume fraction of water inside the polymer) and calculated values using concentration dependent (full curve) and constant (dotted curve) interaction parameters as a function of the volume fraction of water in the liquid feed, for the system water—ethanol—cellulose acetate.

From the calculated values when using constant polymer—nonsolvent interaction parameters, an inversion of the preferential sorption can be observed which is not in agreement with the experimental observations. To improve agreement between the experimental and theoretical values, concentration dependent g_{13} and g_{23} parameters have been used. By investigating the effect of the constants a, b, c and d (see eqns. 15 and 16) on the preferential sorption, it became clear that a reasonable agreement between theory and experiment was obtained when the coefficient a has a higher value than c. The concentration dependence of g_{13} and g_{23} is given in Fig. 6.

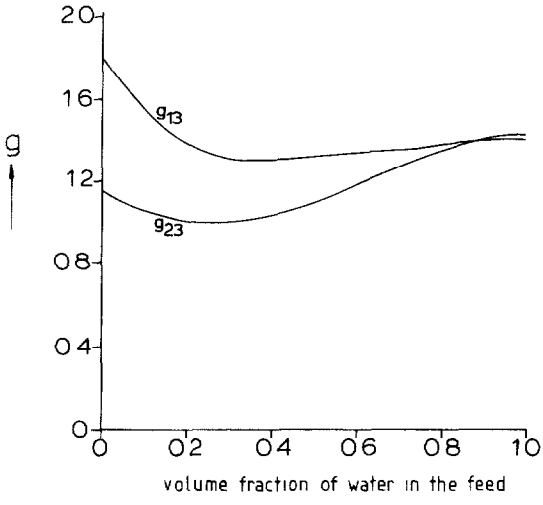

Fig. 6. Interaction parameters g_{13} and g_{23} in the system water—ethanol—cellulose acetate as a function of the water concentration in the feed. Parameters used in eqns. (15) and (16) are: $a = 0.6$; $b = 2.2$; $c = 0.1$; $d = 2.2$.

The influence of the g_{13} and g_{23} parameters on the preferential sorption is caused to a large extent by their derivatives and the choice of the coefficients a and c. Hence $a > c$ results in $\partial g_{13}/\partial u_2 > \partial g_{23}/\partial u_1$ which has a positive effect on the preferential sorption of water (see eqn. 11).

The system water—ethanol—polyacrylonitrile (sorption results)

The experimental and theoretical values for the preferential sorption are given in Fig. 7. The theoretical values have been calculated according to eqn. (11) using constant interaction parameters given in Table 1 ($g_{13} = \chi_{13} = 1.8$ and $g_{23} = \chi_{23} = 4.2$).

For low water concentrations in the feed no experimental values could be obtained because the amount of sorbed liquid was too small (see Fig. 2). From Fig. 7 very high values for the preferential sorption of water can be observed. This behaviour could already be expected because of the smaller molar volume of water and the much higher affinity between water and poly-

acrylonitrile in comparison with ethanol and polyacrylonitrile. The theoretical values hardly change when concentration dependent g_{13} and g_{23} parameters were used. Because of the very high fractional water content inside the membrane, the value of g_{13} will not change very much ($u_2 \rightarrow 0$, see eqn. 15) while a higher value of g_{23} has no influence on the preferential sorption.

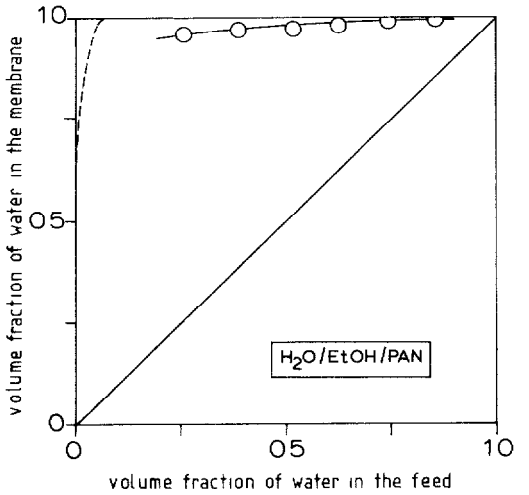

Fig. 7. Experimental (○) and theoretical (---) values for the preferential sorption in the system water—ethanol—polyacrylonitrile as a function of the volume fraction of water in the liquid feed.

The system water—ethanol—polysulfone (sorption results)

This system is a very interesting one because the effect of the difference in molar volumes, contributing to a large extent to the preferential sorption of water in the two other systems studied, is opposed here by the very small mutual affinity between water and polysulfone.

Because a very small amount of liquid is sorbed by polysulfone, especially at high water concentrations in the feed, only one experimental value has been obtained at a high ethanol feed concentration. The theoretical and experimental results are given in Table 2.

TABLE 2

Theoretical and experimental value of preferential sorption in the system water—ethanol—polysulfone

	Water in feed (v_1) (weight fraction)	Water in membrane (u_1) (weight fraction)
Experimental	0.11	0.23
Theoretical	0.11	0.28

Parameters used in eqns. (15) and (16) are: $a = 0.2$; $b = 65.0$; $c = 1.2$; $d = 65.0$.

Using concentration independent interaction parameters, the term $l\chi_{23} - \chi_{13}$ (= −5.1) which is very large, dominates completely and predicts a preferential sorption of component 2 (ethanol). By taking the interaction parameters concentration dependent, preferential sorption of water can be calculated. However, the coefficients a, b, c and d (see eqns. 15 and 16) have completely different values as in the case of cellulose acetate. Although a reasonable agreement can be obtained between theory and experiment, the physical interpretation of the values for the coefficients a, b, c and d is still unexplained. Nevertheless, it is striking that even in hydrophobic polymers such as polysulfone, water is sorbed preferentially.

Preferential sorption versus preferential permeation

The main objective of this paper was to investigate preferential sorption in relation to selective transport in pervaporation. Successively, we will discuss the systems water—ethanol—cellulose acetate, water—ethanol—polyacrylonitrile and water—ethanol—polysulfone.

The system water—ethanol—cellulose acetate (sorption vs. permeability)

In Fig. 8 the experimental sorption values and the results for pervaporation are given as a function of the weight fraction of water in the feed mixture. It is obvious that both curves show practically the same behaviour. If these results are considered in terms of the solution—diffusion model, where the flux of a component through a membrane is a function of solubility, S, and

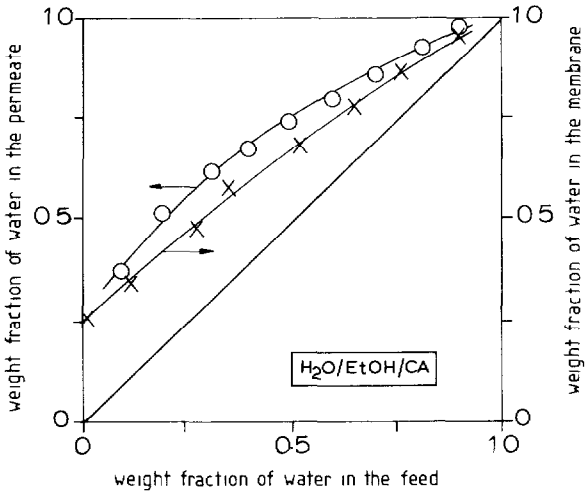

Fig. 8. Experimental values for preferential sorption (expressed as weight fraction of water inside the polymer) and for pervaporation (expressed as weight fraction of water in the permeate) for the system water—ethanol—cellulose acetate as a function of the weight fraction of water in the feed.

diffusivity, D, it is clear that solubility contributes to a major part to selective transport

$$\frac{J_1}{J_2} = \frac{S_1(c_1, c_2)}{S_2(c_1, c_2)} \quad \frac{D_1(c_1, c_2)}{D_2(c_1, c_2)} \tag{17}$$

In the case of water and ethanol permeating through cellulose acetate, both the ratios S_1/S_2 and D_1/D_2 are larger than one. For water and ethanol the ratio D_1/D_2 is larger than one because of the difference in size of the molecules (see for instance Berens [16]). So in order to obtain very high selectivities the ratios S_1/S_2 and/or D_1/D_2 should be very large. For the system water—ethanol—cellulose acetate the ratio S_1/S_2 is rather low and moderate selectivities are obtained, implying that the ratio D_1/D_2 will not be very large either.

The system water—ethanol—polyacrylonitrile (sorption vs. permeability)

For this system the experimental preferential sorption values and the results for pervaporation as a function of the weight fraction of water in the feed are given in Fig. 9. Again, both curves show the same behaviour.

Because the ratio S_1/S_2 is much larger here compared to that for cellulose acetate, very high selectivities could be expected and are indeed achieved. For this system also, the contribution of the preferential sorption to the selectivity in permeation turns out to be the leading factor.

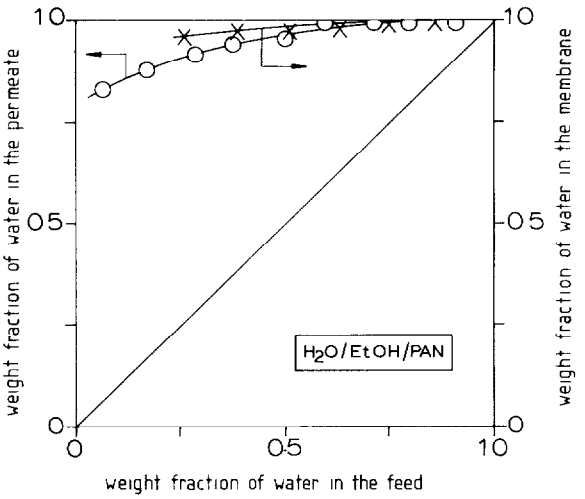

Fig. 9. Experimental values for preferential sorption and pervaporation for the system water—ethanol—polyacrylonitrile as a function of the weight fraction of water in the feed.

The system water—ethanol—polysulfone (sorption vs. permeability)

In a previous section it was shown that water is sorbed preferentially from an ethanol—water mixture in the strongly hydrophobic polymer polysulfone. Analogous to the other systems studied, a preferential permeability for water

should be expected. In Fig. 10, the one experimental sorption value and a curve for pervaporation results are given as a function of the weight fraction of water in the liquid feed. As was found for the other two systems, preferential sorption and preferential permeation show parallel behaviour, but in contrast to the other two systems, the sorption selectivity is much lower than the selectivities found in the pervaporation process. We think that in this system the mobility of the ethanol molecules has been decreased because of the hydrophobic interactions between ethanol and polysulfone. As a consequence the ratio D_1/D_2 should be very large.

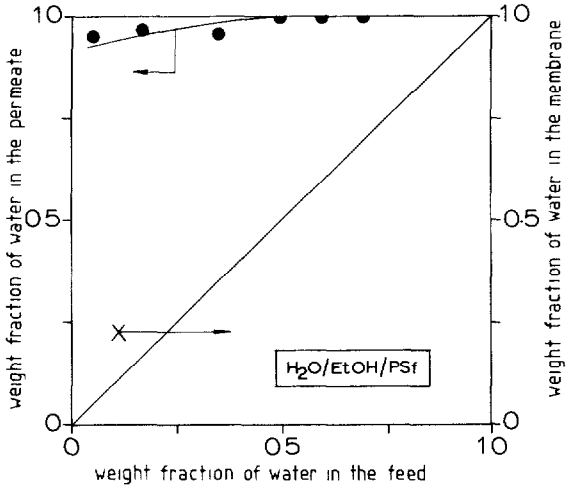

Fig. 10. Experimental values for preferential sorption (one point, ×) and pervaporation for the system water—ethanol—polysulfone as a function of the weight fraction of water in the feed.

The system water—ethanol—polysulfone is a perfect example to demonstrate the presence of coupled transport. For pure water no sorption nor permeation can be observed, while in the presence of ethanol water is sorbed and transported preferentially. In several models [3,17] it has been tried to predict selectivity and permeation rates from parameters obtained from single-component experiments. The results presented here demonstrate clearly that it would be hardly possible to predict membrane characteristics for non-ideal mixtures like water—ethanol from single-component experiments only. Coupling occurs in the thermodynamic part ("solution") as well as in the kinetic part ("diffusion") of the solution—diffusion mechanism.

Another interesting aspect which can be deduced from our experiments is that the assumption of ideal sorption behaviour cannot be used for non-ideal mixtures such as ethanol—water. This can be demonstrated clearly by the system water—ethanol—polysulfone (but also by the other two systems). Krewinghaus [18] assumed a linear relationship (ideal sorption) between the

concentration of a compound in the membrane and the concentration of that component outside the membrane, according to eqn. (18)

$$c_i = x_i\, c_i^o \tag{18}$$

where c_i is the concentration of component i in the membrane, x_i is the mole fraction of component i in the liquid feed mixture and c_i^o is the solubility in the membrane for the pure component. Equation (18) cannot be used for the system water—ethanol—polysulfone, because for pure water there is no sorption in a polysulfone membrane while in the presence of ethanol, water is sorbed preferentially. In general, one can say that in cases where preferential sorption occurs eqn. (18) cannot be used.

Conclusions

Using Flory—Huggins thermodynamics, extended with concentration dependent interaction parameters, the agreement between theoretical and experimental values for the preferential sorption of low molecular weight components in polymeric membranes is reasonably well established. For the systems studied, preferential sorption of water from ethanol—water mixtures occurs, and this can be ascribed to the large difference in molar volume between water and ethanol. Comparison of the preferential sorption values and the results for preferential permeation show that preferential sorption of water contributes to a large extent to selective water transport. From the results presented here it can be predicted that high selectivities for water from ethanol—water mixtures can be expected when the total amount of liquid inside the polymer is small (in this case the permeation rates will be low, however), and when the affinity between water and polymer is larger than that between ethanol and polymer.

In terms of the solution—diffusion model the conclusion is justified that the component that is sorbed preferentially will also permeate preferentially. This statement is in agreement with the observations of Aptel [5]. Furthermore it can be concluded that the assumption of ideal sorption cannot be used in general.

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List of symbols

a	activity
c	concentration inside the membrane
c^o	solubility of the pure component in the membrane
CR	composition ratio

g	concentration dependent interaction parameter
ΔG_{mix}	free energy of mixing (J-mol^{-1})
ΔG^E	excess free energy of mixing (J-mol^{-1})
l	ratio of molar volumes (= V_1/V_2)
n	mole fraction in the ternary phase
P	pressure (Pa)
R	gas constant (J-mol^{-1}-K^{-1})
T	temperature (K)
u	volume fraction confined to the nonsolvent part in the ternary phase
v	volume fraction in the binary phase
V	molar volume (cm^3-mol^{-1})
x	mole fraction in the binary phase
ϵ	coefficient of preferential sorption
χ	concentration independent binary interaction parameter
ϕ	volume fraction in the ternary system
μ	chemical potential (J-mol^{-1})
Π	osmotic pressure (J-cm^{-3})

Indices

1	water
2	ethanol
3	polymer
i	component i
m	membrane

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